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Separation of asymmetric quadricovalent phosphonium bases into optically active components.

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The resolution of RR'R"R"'PX into optically active forms is reported. For prepn. of the necessary asymmetric tertiary phosphines, the following quaternary salts were prepd.: $Et_2Ph(PhCH_2)PCl$, m.194-5°; $Et_2Bu(PhCH_2)PCl$, m.148-9°; $Pr_2Ph(PhCH_2)PCl$, m.134-5°; $Pr_2Bu(PhCH_2)PCl$, m.154.5-5.0°; $Bu_2Ph(PhCH_2)PCl$, m.156-7°. Thermal decompn. of these in CO_2 atm. gave asymmetric phosphines: $EtPh(PhCH_2)P$, b_{15} 165-8°, d_{20} 1.0393, n_D^{20} 1.5960; $PrPh(PhCH_2)P$, b_{12} 172-5°, n_D^{20} 1.5680; $BuPh(PhCH_2)P$, b_{11} 184-90°, d_{20} 1.0112, n_D^{20} 1.5729; $EtBu(PhCH_2)P$, b_6 135-9°, d_{20} 0.9338, n_D^{20} 1.5310; $PrBu(PhCH_2)P$, b_1 113-15°, d_{20} 0.09467, n_D^{20} 1.5090. Their formation proceeded with evolution of olefins, HCl and $PhCH_2Cl$. Reaction of these phosphines with $CH_2:CHCH_2Br$ and BuBr gave the following phosphonium salts: $Et(PhCH_2)(CH_2:CHCH_2)_2PBr$, m.148-50°; $EtBuPh(PhCH_2)PBr$, m.141-2°; $EtBu(CH_2:CHCH_2)(PhCH_2)PBr$, m.87-9°; $PrPh(PhCH_2)(CH_2:CHCH_2)PBr$, m.153-4°; $BuPh(CH_2:CHCH_2)(PhCH_2)PBr$, m.102-2.5°. When these salts were treated with Ag d-π-bromocamphorsulfonate only 2 crystalline bromocamphorsulfonates were obtained: $EtPh(PhCH_2)(CH_2:CHCH_2)P$ (I), and $BuPh(PhCH_2)(CH_2:CHCH_2)P$ (II); the others formed sirups. I was taken up in EtOAc and the solvent was partly evapd., yielding a crop of crystals of I, m.148-50°. Further fractions were obtained by evapn. of the solvent, with $[\alpha]_D$ changing from 53.6° to 38.8° in the last fraction. When II, m.141-2°, was similarly crystallized, no sepn. occurred and $[\alpha]_D$ remained at 44.1-45°. Attempts to convert I and II into crystalline bromides which could be resolved were fruitless.

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